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Adsorption of nicosulfuron herbicide in the agricultural soils of Bosnia and Herzegovina

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Abstract: In this study, the sorption characteristics of nicosulfuron herbicide in soils from different agricultural regions of Bosnia and Herzegovina, as well as factors influencing the sorption process, were evaluated. The analysis was performed using a batch equilibrium method. The obtained results showed that soils in Bosnia and Herzegovina are very versatile in terms of their characteristics. The Freundlich adsorption coefficient (K_f) coefficient ranged from 0.027 to 7.388, while the slope of the Freundlich isotherm ($1/n$) varied from 0.291 to 1.927. In soils with pH 4.31–7.60, $1/n$ was found to be less than 1 (0.337–0.547), and for the extremely alkaline soil with pH 8.2, $1/n$ was 1.927. Adsorption of nicosulfuron in the tested soils of Bosnia and Herzegovina was significantly correlated with the sand and silt content in the soil. Multiple linear regression correlating log K_f with the sand and silt content in the studied soils was also statistically significant (R^2 = 0.951; P = 0.0108). The results of this study indicate that in sandy soils, which are slightly or moderately alkaline, the adsorption of nicosulfuron is very low and only a small amount of nicosulfuron will be adsorbed.

Keywords: sulfonylurea; leaching potential; physico-chemical properties

Maize (*Zea mays* L.) is a dominant crop in the agricultural regions of Bosnia and Herzegovina (B&H). However, contemporary maize production requires appropriate plant protection, including intensive application of plant protection products. The most applied herbicide in maize is sulfonylurea herbicide nicosulfuron (2-[(4,6-dimethoxypyrimidine-2-ylcarbamoyl)sulfamoyl]-N,N-dimethylnicotinamide) (McBean 2012). Sulfonylureas, including nicosulfuron, are highly effective in very low concentrations; however, the low application rate does not guarantee low environmental risks. Their residues could be present in soil and through the leaching process, could enter groundwater. Persistence of these residual herbicides and their metabolites can affect sensitive plant species during crop rotations, causing phytotoxicity. For most herbicides, the content of soil organic matter and soil texture are the major factors affecting their phytotoxicity and persistence in soil (Rahman et al. 2011), while the main process controlling herbicide movement in soil is sorption.

Knowledge of the fate and behavior of the compound being intensely applied is of great importance, since soil and water pollution are significantly influenced by the adsorption capacity of pesticides for soils.

The soil adsorption coefficient (K_d), defined as the ratio of the amount of pesticide adsorbed to the soil and the amounts remaining in the soil solution

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under equilibrium distribution conditions, is a basic measure of the pesticide adsorption. K_d is a measure of binding of a given compound to a soil type and its value is highly influenced by physicochemical properties of the soil. Adsorption of herbicides from soil solution to soil colloids results in a decrease in its concentration in the solution and it is characterised by an absorption coefficient. High K_d values indicate that the herbicide is highly adsorptive and therefore it is immobile in soil and resistant to microbial degradation (Beulke et al. 2004). Parameters Freundlich adsorption coefficient (K_f) and $1/n$ from the Freundlich isotherm are often used to explain the mechanisms of adsorption of pesticides in soil (Sparks 2003).

The majority of maize production in Bosnia and Herzegovina is concentrated in the valley of the Vrbas and Sava rivers. In these areas, the level of groundwater is high and the risk of potential contamination from the agricultural activity is more expressed.

Moderate to high mobility of nicosulfuron in soil (sorption coefficient normalised to soil organic carbon content (K_{oc}) < 100 mL/g), and a weak acid with pK_a 4.6 (Brown 1990), classify nicosulfuron into the herbicides with a potential for water contamination. Due to the high GUS (groundwater ubiquity score) index, its presence has also been established in groundwater (Battaglin et al. 2000). Pesticide presence in groundwater is highly influenced by their mobility, while the sorption coefficient and K_{oc} are the most frequently used for this estimation.

Recently, numerous studies have been conducted on this topic, including different sulphonylurea herbicides. Freundlich coefficients for sorption of bensulfuron-methyl on non-amended and amended soils were in the range 0.18–0.41 (K_f) and 0.74–1.01 ($1/n$) (Delgado-Moreno and Peña 2007), while for triasulfuron K_f and $1/n$ were in the interval 0.08–0.20 and 0.47–0.86, respectively (Said-Pullicino et al. 2004). Nicosulfuron adsorption studies in the soils of Brazil and Iowa found that K_f varied, depending on the soil type, from 0.21 to 8.78, while $1/n$ ranged from 0.69 to 1.00 (Gonzales and Ukrainczyk 1996). Liu et al. (2012) reported that K_f and $1/n$ values of nicosulfuron in five soils were 0.42–6.58 and 0.92–1.14, respectively. However, there is a lack of data regarding sorption study of pesticides in soils of B&H.

The aim of this study was to evaluate the sorption characteristics of nicosulfuron herbicide in soils from different agricultural regions in Bosnia and Herzegovina, as well as the factors influencing this process.

MATERIAL AND METHODS

Soil samples. For the sorption study, six soil samples (0–10 cm) were collected from different areas of Bosnia and Herzegovina, with the most intensive agriculture production. Before the analysis, soil samples were air-dried, milled and sieved through a 2 mm sieve. Soil texture was analysed by the traditional method with 0.1 mol/L Na-pyrophosphate. The determination of soil organic carbon is based on the wet oxidation method, using potassium dichromate as the oxidizing agent (Predić et al. 2019).

Adsorption experiment. The Freundlich constant was determined for all six soil samples (n = 3). Soil samples (3 g) were enriched with nicosulfuron standard solution (6 mL) in four concentrations within the range of 0.005415–0.04332 mg/mL. After vortexing (30 s), samples were placed in a horizontal shaker for equilibration (24 h) at room temperature and afterwards, samples were centrifuged at 6 000 rpm for 15 min. The supernatant was filtered through a 0.45 μm nylon filter and the content of nicosulfuron was determined.

In order to evaluate if all the nicosulfuron residues were in the soil, the experiment was made by adding 6 mL of acetonitrile to the soil and then vortexing for 30 s, shaking again for 24 h and repeating centrifugation, filtration and HPLC (high-performance liquid chromatography) analysis. It was determined that a portion absorbed into the soil together with the pesticide portion in the aqueous phase makes up 100%.

Chemicals and HPLC analysis. The analytical standard of nicosulfuron (96%) was obtained from Dr. Ehrenstorfer, Germany. Acetonitrile, HPLC grade, was purchased from "J. T. Baker" (Darmstadt, Germany), while ultrapure water was obtained from Merck (Milan, Italy).

For the analysis of nicosulfuron content, HPLC-DAD (Agilent 1260 Infinity), equipped with EC-C18 (Poroshell-120, 4.6 × 50 mm, 2.7 μm) column was used. The mobile phase was acetonitrile (70%) and acidified (0.1% HAc) ultrapure water (30%), with isocratic elution and a flow rate of 0.55 mL/min. Injected volume was 10 μL, column temperature 25 °C, while the detection wavelength was 245 nm. Under these conditions, the retention time of nicosulfuron was 1.038 min.

RESULTS AND DISCUSSION

Nicosulfuron adsorption study was performed on 6 different soil types. The physical and chemical properties of the analysed soils are shown in Tables 1

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Table 1. Physical properties of the soils

Soil	Sample No.	Mechanical composition			Textural classification
		sand (2.0–0.06 mm) (%)	silt (0.06–0.002 mm) (%)	clay (< 0.002 mm) (%)	
1	209 (PC6SC)	10.70	49.00	40.30	silty clay
2	231 (SS5SCL)	1.90	60.50	37.60	silty clay loam
3	296 (GTL4SL)	25.00	61.20	13.80	silty loam
4	301 (CEL7SL)	10.10	70.09	19.81	silty loam
5	306 (SNJ5SL)	9.90	71.90	18.20	silty loam
6	1367 (TMP8SL)	68.20	16.30	15.50	sandy loam

and 2. Correlation between nicosulfuron sorption parameters and nicosulfuron content in the liquid phase was obtained by linear regression, i.e. the Freundlich adsorption isotherm:

$$x/\text{m} = K_\text{f}\,(\text{C}_\text{aq})^{1/n} \text{ or } \log x/\text{m} = \log K_\text{f} + 1/n \log \text{C}_\text{aq}$$

where: x/m – concentration of the pesticide sorbed to the soil; C_aq – concentration in water, $1/n$ and K_f the power coefficient and the Freundlich constant calculated from the slope and the intercept respectively (Capri 2001, Wauchope et al. 2002). Results are presented in Table 3, Figures 1 and 2.

Freundlich parameters of adsorption of nicosulfuron for the studied soils ranged from 0.027 to 7.388, while the $1/n$ was between 0.291 to 1.927. In soils with pH 4.31–7.60, $1/n$ was less than 1, ranging from 0.337 to 0.547, indicating that the adsorption isotherm of nicosulfuron in these soils was of the L-type. It is a convex curve, curved upwards, where the marginal sorption energy decreases with increasing surface concentration (Delle Site 2001). In this case, the relative adsorption of nicosulfuron decreases with the increase of its concentration. However, for the highly alkaline soil (6) with pH 8.2, $1/n$ was 1.927, indicating the S-type isotherm, that is, a concave curve curved upwards, at which marginal sorption energy increases with increasing surface concentration (Delle Site 2001). This can be explained by the fact that at pH 8.2, most of the nicosulfuron molecules were negatively charged and therefore a very small percentage of nicosulfuron was adsorbed.

Correlations between the adsorption indicators for nicosulfuron (logK_f, K_f, $1/n$ and n) and physico-chemical properties and mechanical composition of the soil are presented in Tables 4 and 5.

The results of the linear correlation indicate that the adsorption of nicosulfuron in the tested soils is statistical significantly dependent on the sand content and silt dust in the soil, where the linear correlation coefficients between K_f and logK_f, and the sand content are negative (Table 4). On the contrary, correlations between K_f and logK_f and the silt content were both positive. Although the correlation coefficient was positive (0.562), no significant interactions among K_f and clay content were set.

Multiple linear regression analysis between of K_f (logK_f) and the sand and silt content of the tested soils was obtained by using following equations:

$$K_\text{f} = 7.384 - 0.1036 \times \text{sand} + 0.0186 \times \text{silt}$$
$$(R^2 = 0.861;\ P = 0.052;\ n = 6)$$

$$\log K_\text{f} = 0.239 - 0.0279 \times \text{sand} + 0.012 \times \text{silt}$$
$$(R^2 = 0.951^*;\ P = 0.0108;\ n = 6)$$

Table 2. Chemical properties of the soils

Soil	CEC (mmol$_+$/100 g soil)	$\text{pH}_{\text{H}_2\text{O}}$	pH_KCl	OC (%)
1	47.30	6.70	5.40	2.20
2	43.55	5.91	4.33	1.97
3	27.90	4.31	3.85	2.26
4	32.65	7.60	6.70	1.86
5	24.80	5.13	4.01	1.86
6	15.00	8.20	7.50	1.86

CEC – cation exchange capacity; OC – organic carbon

Table 3. Freundlich parameters for adsorption of nicosulfuron for the studied soils

Soil	K_f (μg$^{1-1/n}$mL$^{1/n}$/g)	logK_f	$1/n$	R^2
1	4.369	0.640	0.337	0.908
2	7.388	0.868	0.379	0.827
3	4.374	0.641	0.291	0.692
4	4.625	0.665	0.471	0.873
5	4.355	0.639	0.547	0.887
6	0.027	–1.569	1.927	0.834

K_f – Freundlich adsorption coefficient; $1/n$ – Freundlich power coefficient

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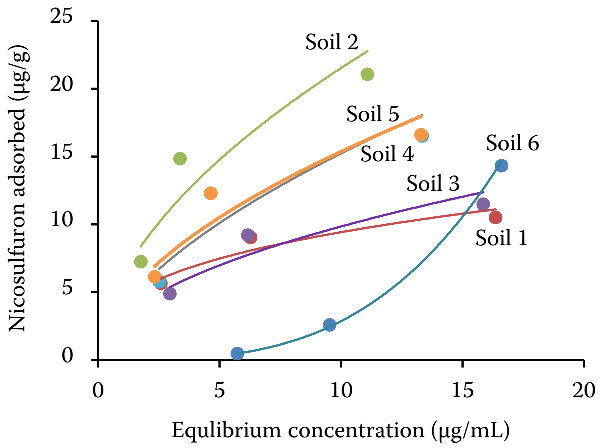

Figure 1. Adsorption isotherms of nicosulfuron on soils

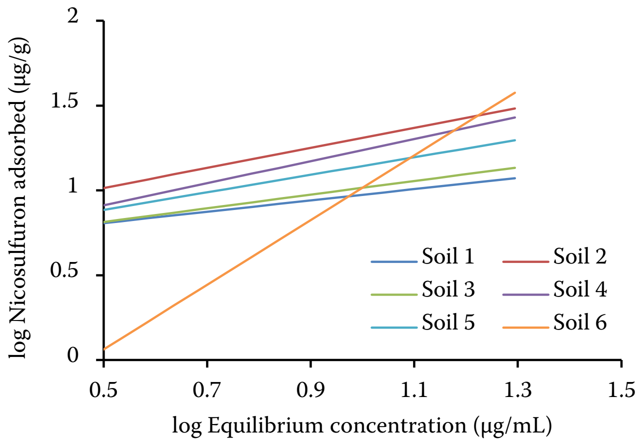

Figure 2. Freundlich adsorption isotherms nicosulfuron by soils

Correlations between K_f and logK_f, and pH_{H_2O} were negative (–0.618 and –0.52), and these correlations with pH_{KCl} were even stronger (–0.717 and –0.676) (Table 4). This indicated that soils with higher pH had lower sorption capacity, as already confirmed by other studies (Kah and Brown 2006, Grahovac et al. 2017). The obtained correlations were expected, because the sorption of slightly acidic herbicides, such as nicosulfuron, increases with decreasing soil pH. The greatest effect on herbicide sorption, regarding soil physicochemical properties, are that of organic carbon (OC) content, pH and clay content (Azcarate et al. 2015). Sorption increases with increasing OC and decreasing pH ($P > 0.05$). Different studies about the correlation between sulfonylureas (SUs) sorption and OC content produced contradictory results, and no correlation between the clay content and sorption of the tested SUs was found (Azcarate et al. 2015). This could be due to different pH of the tested soils, because pH may reduce the effect of OC content on the sorption of sulfonylureas. Sulfonylureas are weak acids and are generally found in the anionic form in soils with pH higher than the pK_a. As the soil pH increases, participation of neutral forms of the herbicide molecules decreases and lower sorption can be expected (Oliveira et al. 2001, Kah and Brown 2006). According to Grahovac et al. (2017) numerous studies related to weakly acidic herbicides, including nicosulfuron, reported negative interaction among herbicide sorption and soil pH, i.e. sorption of slightly acidic herbicides increases as soil pH decreases. Ahmad et al. (2016) reported that maximum adsorption of chlorosulfuron in soil was observed at low pH and minimum at high pH. According to the available data, this is the first study of nicosulfuron sorption potential of soils in Bosnia and Herzegovina.

In recent years, a number of studies worldwide dealt with the behaviour of nicosulfuron in different soils. K_d for nicosulfuron in the Argentinian soils (0.02 to 0.47) (Azcarate et al. 2015) was lower than those found by Oliveira et al. (2001), where K_d ranged from 0.14 to 1.38. On the other hand, K_d for nicosulfuron in the biochars was 0.00, that is, no sorption of nicosulfuron was observed on the

Table 4. Correlation matrix (Pearson correlation coefficient, r) for nicosulfuron adsorption parameters and physical properties of the soils

Adsorption indicator		Sand	Silt	Clay
logK_f	r	–0.967**	0.910*	0.411
	P	0.002	0.012	0.418
K_f	r	–0.924**	0.775	0.562
	P	0.008	0.070	0.246
1/n	r	0.921**	–0.861*	–0.402
	P	0.009	0.027	0.430

*$P < 0.05$; **$P < 0.01$

Table 5. Correlation matrix (Pearson correlation coefficient, r) for nicosulfuron adsorption parameters and chemical properties of the soils

Adsorption indicator		pH_{H_2O}	pH_{KCl}	CEC	OC (%)
logK_f	r	–0.618	–0.717	0.716	0.324
	P	0.190	0.108	0.110	0.531
K_f	r	–0.520	–0.676	0.765	0.201
	P	0.290	0.140	0.076	0.702
1/n	r	0.647	0.722	–0.728	–0.487
	P	0.165	0.105	0.101	0.348

CEC – cation exchange capacity; OC – organic carbon

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biochars, which may be due to the higher repulsion of anionic molecules (> 99%) (Trigo et al. 2014).

According to Gonzales and Ukrainczyk (1996), K_f was highly significant (P < 0.001) and positively correlated with cation exchange capacit (CEC) (r = 0.83), and 1/n was also positively correlated with CEC, with a correlation coefficient of 0.71 (P < 0.01). Correlation between K_f and pH of Brazilian soils was –0.94*, while for Iowa soils it was –0.39. Correlation between K_f and clay content of Iowa soils was 0.78*, while for Brazilian soils this correlation was negative with the correlation coefficient –0.52. This shows the complexity of the herbicide adsorption studies, and the importance of determining mineral composition of clay. Studying of the adsorption of nicosulfuron in Brazilian soils showed an interaction among K_d (L/kg) and the clay content (%) of 0.503, while K_d correlations with pH and CEC ($cmol_+$/kg) were 0.351 and 0.802, respectively (Oliviera et al. 2001). In the analysis of nicosulfuron sorption conducted with American, Brazilian and Hawaiian soils, K_f value varied from 0.14 to 1.69 and 1/n ranged from 0.92 to 0.97 (Regitano and Koskinen 2008).

The results of this study indicate that in sandy soils, which are slightly to moderately alkaline, the adsorption of nicosulfuron is very low and only a small amount of nicosulfuron will be adsorbed in soil particles. This requires limiting the use of nicosulfuron, due to the possibility of leaching into groundwater. Since in Bosnia and Herzegovina karst fields occupy about 100 000 ha, with sandy and slightly to moderately alkaline soils, the use of nicosulfuron, as well as similar acidic herbicides, must be in accordance with the sustainable use of pesticides, including the risk assessment for a particular region.

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